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1. REPORT DATE (DD-MM-YYYY) 21-10-2010		2. REPORT TYPE Technical Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE  Packing Fraction and Relation to Glass Transition in Ternary Blends of Cyanate Ester Resins				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Andrew J. Guenthner, Joseph M. Mabry (AFRL/RZSM); Kevin R. Lamison, Vadana Vij (ERC)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 23030521	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/RZSM 9 Antares Road Edwards AFB CA 93524-7401				8. PERFORMING ORGANIZATION REPORT NUMBER  AFRL-RZ-ED-TP-2010-434	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-70448				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2010-434	
12. DISTRIBUTION / AVAILABILITY STATEMENT  Approved for public release; distribution unlimited (PA #10531).					
13. SUPPLEMENTARY NOTES For presentation at the American Chemical Society Spring 2011 National Conference, Anaheim, CA, 37-31 Mar 2011; for publication in Polymeric Materials Science and Engineering Preprints.					
14. ABSTRACT Studies of copolymerized blends of dicyanate esters revealed systematic deviations from a simple rule of mixtures for both the packing fraction and the dry glass transition temperature. These deviations are high correlated, with a lower packing fraction corresponding to a higher dry T <sub>g</sub> . The correlation appears to result from differences in the degree of cure achieved in the various blend samples, with a higher degree of cure producing both a higher dry T <sub>g</sub> as well as a lower packing fraction, in accordance with the known physical properties of cyanate ester resins.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT  SAR	18. NUMBER OF PAGES  4	19a. NAME OF RESPONSIBLE PERSON Dr. Joseph M. Mabry
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

## **Packing Fraction and Relation to Glass Transition in Ternary Blends of Cyanate Ester Resins**

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To be presented at the ACS National Meeting, Anaheim, CA, March 20, 2011, with the accompanying abstract and separate preprint

### **Abstract**

Studies of copolymerized blends of dicyanate esters revealed systematic deviations from a simple rule of mixtures for both the packing fraction and the dry glass transition temperature. These deviations are highly correlated, with a lower packing fraction corresponding to a higher dry  $T_g$ . The correlation appears to result from differences in the degree of cure achieved in the various blend samples, with a higher degree of cure producing both a higher dry  $T_g$  as well as a lower packing fraction, in accordance with the known physical properties of cyanate ester resins.



# Packing Fraction and Relation to Glass Transition in Ternary Blends of Cyanate Ester Resins

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## INTRODUCTION

Polycyanurates (or "cyanate ester resins") have become an important class of thermosets, offering advantages in aerospace, energy, and electronics applications<sup>1-3</sup>. Cured cyanate esters offer many desirable properties compared to similarly prepared epoxy resin systems, including improved fire resistance<sup>4</sup>, increased service temperature<sup>5</sup>, and reduced water uptake<sup>6</sup>. Monomer handling is simplified by the fact that these materials exhibit low toxicity, minimal shrinkage and out-gassing on cure, and are generally suitable for blending with co-monomers<sup>7</sup> and toughening additives<sup>8</sup>.

The van der Waals ( $V_w$ ) volume is the space truly occupied by the atoms of that molecule<sup>9</sup>. This volume is impenetrable to non-bonded atoms and molecules. Comparatively, the molar volume ( $M_v$ ) is given by the space occupied by one mole of the material. This value is readily accessible from the density and molecular weight of the material. The packing fraction ( $P_f$ ) is the ratio of the  $V_w$  to the  $M_v$ . This value can be described as the portion of a material's volume actually occupied by atoms.

## EXPERIMENTAL

**Materials.** Bisphenol A dicyanate ester (Primaset® BADCy) and Bisphenol E dicyanate ester (Primaset® LECy) were purchased from Lonza and used as received. SiMCy, an analog of BADCy containing a silicon atom in place of the quaternary carbon, was synthesized following previously outlined procedures<sup>9</sup>. Copper (II) acetylacetonate was obtained from ROC/RIC and nonylphenol (technical grade) was obtained from Aldrich, both were used as received.

**Sample Preparation.** Catalyst batches were prepared by blending 30 weight parts nonylphenol with one weight part copper (II) acetylacetonate at 60 °C until dissolved. Batches were discarded after 30 days. Cyanate esters were mixed and degassed at 95 °C for 30 minutes at 300 mm Hg. The samples were then poured into clean cylindrical silicone molds preheated to 95 °C. The cure cycle was 1 hour at 150 °C followed by 24 hours at 210 °C. Ramp rates between the long dwells were ~5 °C/min. Further details on the cure and mold preparation have been published elsewhere<sup>10</sup>.

**Characterization.** Density of the cured samples was determined using solutions of  $\text{CaCl}_2$  (dihydrate) in deionized water. Discs of the cured cyanate ester were placed into a vessel and two solutions, at different concentrations, were combined until a neutrally buoyant solution was realized. The density of the neutral solution was obtained by weighing a 10.00 mL volumetric flask containing the fluid. This value was compared to the expected density of a  $\text{CaCl}_2$  solution at the known concentration and ambient conditions.

Differential scanning calorimetry (DSC) was performed on ~5 mg of the sample following degassing. Using a TA Instruments Q2000, under 50 mL/min nitrogen purge, each sample was heated to 350 °C, then cooled to 100 °C, and finally heated to 350 °C. All ramp rates were 10 °C/min.

Thermomechanical analysis was performed on TA Instruments Q400 series using the standard cylindrical probe. A preload force of 0.2 N was used to keep the sample discs in place. Force modulation of amplitude 0.1 N at a frequency of 0.05 Hz (maintaining an average force of 0.1 N) was used to investigate the samples. To determine thermal lag, the temperature was cycled between 100 °C and 200 °C at 10 °C/min twice. Generally, the observed thermal lag was between 3-10 °C. Reported values have been corrected to reflect this. After the

cycling, each sample was heated to 350 °C at 10 °C/min. Further information on the TMA testing and analysis are provided elsewhere<sup>10</sup>.

## RESULTS AND DISCUSSION

The blend compositions and corresponding densities obtained from neutral buoyancy testing are shown in Table 1. A small correction factor (~.005 g/cc) was used to account for the 2 phr nonylphenol at a density of .9 g/cc. The density is necessary to calculate the molar volume of the samples.

Table 1. Weight Percent and Densities of Compositions

	BADCy (Percent)	LECy (Percent)	SiMCy (Percent)	Density (g/cc)
BADCy	100	0	0	1.207
LECy	0	100	0	1.226
SiMCy	0	0	100	1.178
Mix 1	68	17	15	1.201
Mix 2	75	0	25	1.193
Mix 3	0	75	25	1.217
Mix 4	17	17	67	1.195
Mix 5	75	25	0	1.214

Table 2 contains several parameters of interest. The first column shows the van der Waals volume ( $V_w$ ) of the blend, which was calculated using the topological method<sup>9</sup>. The next column refers to the number average molecular weight ( $M_w$ ) of the blend. This was calculated based on the known molecular weight of the pure samples. The third piece of data is the molar volume. This value was obtained by dividing  $M_w$  by the density from the table above. The next column is the packing fraction. This value was calculated by dividing  $V_w$  by  $M_v$ . The column labeled deviation shows the difference between the calculated value of the packing fraction based on observed densities and the value based on densities from the volumetric rule of mixing. Thus, for the pure materials, the value is inherently zero. The final column gives the dry  $T_g$  of the blend. This value was obtained from the Tan- $\delta$  curve of the described TMA experiments.

Table 2. Additional Parameters Derived from Density

	$V_w$ (cc/mol)	$M_w$ (g/mol)	$M_v$ (cc/mol)	$P_f$	Deviation	Dry $T_g$ (°C)
BADCy	146	278	231	.631	0	272
LECy	136	264	216	.632	0	288
SiMCy	155	294	250	.621	0	280
Mix 1	145	278	232	.627	-0.003	316
Mix 2	148	282	237	.625	-0.004	306
Mix 3	141	271	223	.631	0.002	252
Mix 4	150	283	237.1	.633	0.002	271
Mix 5	143	275	226.2	.633	0.001	264

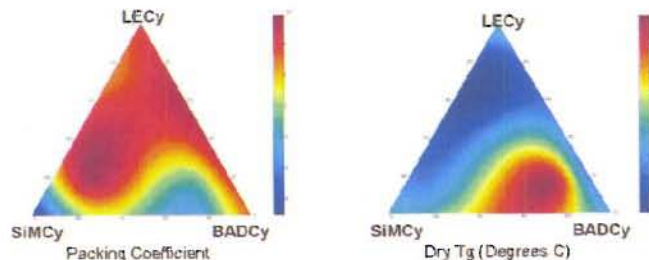


Figure 1. Deviation from average  $P_f$  and Dry  $T_g$  plots for the blends

Figure 1 shows two ternary plots, one describing the variation of the packing coefficient and one illustrating the dry  $T_g$ . On these plots, each vertex refers to a pure sample of material, while the edges are



binary blends of the two connected vertices. The area inside the triangle corresponds to ternary blending. The plot on the left shows the deviation from the average packing value (0.627). Warmer colors correspond to less deviation from the average. The plot on the right shows the  $T_g$  as a function of blend composition. Warmer colors show a higher  $T_g$ .

Lower packing in these cyanate ester systems corresponds strongly to higher  $T_g$ . This is opposite what is predicted by the theory of free volume. However, cyanate esters expand after the gel point during cure<sup>2</sup>. This expansion increases the molar volume with no corresponding change in  $V_w$ , effectively lowering the packing fraction. The molar volume continues to increase with extent of cure, while the  $T_g$  also increases due to further cross-linking. This provides for the correlation between lower packing fraction and higher  $T_g$ .

### CONCLUSIONS

Studies of copolymerized blends of dicyanate esters revealed systematic deviations from a simple rule of mixtures for both the packing fraction and the dry glass transition temperature. These deviations are highly correlated, with a lower packing fraction corresponding to a higher dry  $T_g$ . The correlation appears to result from differences in the degree of cure achieved in the various blend samples, with a higher degree of cure producing both a higher dry  $T_g$  as well as a lower packing fraction, in accordance with the known physical properties of cyanate ester resins.

### ACKNOWLEDGMENT

The support of the Air Force Office of Scientific Research is gratefully appreciated.

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